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Electronic and Ionic Transport in Processable Conducting Polymers

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**ELECTROCHEMICALLY INITIATED CHAIN POLYMERIZATION
OF PYRROLE IN AQUEOUS MEDIA**

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Electrochemically Initiated Chain Polymerization of Pyrrole in Aqueous Media

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Abstract

The electrochemical quartz crystal microbalance has been employed to investigate the electropolymerization of pyrrole in a variety of aqueous electrolytes. In contrast to the generally accepted cation-radical coupling process for the electropolymerization of pyrrole, an electrochemically initiated chain polymerization, featuring a high polymerization rate and involving little charge transport, was found under specific conditions in the presence of ClO_4^- , BF_4^- , and PF_6^- electrolytes. The more typical cation-radical coupling mechanism, characterized by a constant polymerization charge to mass deposited ratio, is observed in the presence of Cl^- , NO_3^- , dodecyl sulfate, copper phthalocyanine tetrasulfonate, β -cyclodextrin tetradecasulfate, and poly(styrene sulfonate). Electrochemical characterizations of polypyrrole films prepared in aqueous ClO_4^- electrolytes reveal that the polymer formed via chain polymerization exhibits the ability to transport both cations and anions during electrochemical switching between redox states, while the polymer synthesized through cation-radical coupling is only capable of transporting a single ionic species.

Introduction

Polypyrrole is one of the most widely studied conducting polymers due to its ease of synthesis, stability in the conducting form, applicability to aqueous (potentially biological) media and overall interesting electrochemical switching properties¹. While many studies have been published in an attempt to elucidate the impact of the electropolymerization process on the structure and properties of polypyrrole²⁻⁸, only a few papers have directly addressed its electropolymerization mechanism⁹⁻¹². This may be due to the fact that common electrochemical methods, including cyclic voltammetry (CV), chronocoulometry, and chronoamperometry, are useful tools for investigating electrochemical reactions but are unable to distinguish the polymerization process occurring on the electrode from the redox events that occur in solution. The difficulty in directly determining the rate of film deposition, and coulombic efficiency of the electropolymerization process, has greatly limited the effectiveness of these techniques. Recently, the electrochemical quartz crystal microbalance technique (EQCM) has proven capable of sensing gravimetric changes on electrode surfaces and has made in situ investigation of electropolymerization and deposition possible. The application of this technique has recently been reviewed¹³⁻¹⁴.

Previously, we reported on the electropolymerization of pyrrole in organic media using the EQCM¹². Due to the obvious practical value of understanding the electrochemical process in different environments, we are interested in the electropolymerization of pyrrole and properties of the resultant polymer in aqueous media. For example, we have recently found that polypyrrole/poly(styrene sulfonate) can bind poly-l-lysine to the film surface in aqueous media, while histone H3 can extract loosely bound poly(styrene sulfonate) chains from the polypyrrole and precipitate as a complex in solution¹⁵⁻¹⁶.

In this paper, we focus on a study of the electropolymerization of pyrrole in a variety of aqueous electrolytes. Our results indicate that, in contrast to the generally accepted cation-radical coupling mechanism for the electropolymerization of pyrrole in many organic and aqueous

electrolyte solutions, electrosynthesis of polypyrrole in the presence of aqueous ClO_4^- , BF_4^- , and PF_6^- electrolytes involves a chain polymerization process.

Experimental

Pyrrole (Aldrich Chemicals) was purified immediately before use by passing it through a microcolumn constructed from a Pasteur pipet, glass wool and activated alumina. This procedure was repeated until a colorless liquid was obtained. Common electrolytes were reagent grade and were used as received. Water used in the experiments was double distilled. All electrolyte/monomer solutions were purged with argon prior to use. Experiments were carried out at room temperature and under the protection of an argon blanket.

The electrosyntheses of polypyrrole films were carried out at 0.8V vs. Ag/AgCl in aqueous solutions of 0.1M pyrrole and 0.1M electrolytes including sodium chloride (NaCl), sodium dodecylsulfate (NaDS), sodium nitrate (NaNO_3), sodium perchlorate (NaClO_4), lithium perchlorate (LiClO_4), sodium tetrafluoroborate (NaBF_4), tetraethylammonium tetrafluoroborate (Et_4NBF_4), potassium hexafluorophosphate (KPF_6), sodium copper phthalocyanine-3,4',4'',4'''-tetrasulfonate (Na_4CuTSP), sodium β -cyclodextrin sulfate (NaCDS), and sodium poly(styrene sulfonate) (NaPSS). The polypyrrole films were washed thoroughly with distilled water to remove excess monomer and analyzed in monomer-free 0.1M electrolyte solutions. Electrochemical analyses were performed after the films were electrochemically cycled for a sufficient period of time to ensure complete ion exchange between the polypyrrole film and various electrolyte solutions.

The EQCM system was used in experiments to simultaneously monitor the current and mass change occurring on the working electrode as the electropolymerization proceeds at constant potential. An AT-cut quartz crystal (Valpey Fisher) with gold key hole was used as an oscillator and working electrode. A Ag/AgCl reference electrode and Pt counter electrode were also employed in the electrochemical cell. Details of the EQCM are documented in previous

literature^{12,17}. The EQCM sensitivity is $18 \text{ ng Hz}^{-1} \text{ cm}^{-2}$ with a working electrode area of 0.71 cm^2 . An HP 8553B spectrum analyzer was employed to measure the conductance peak width of the resonant frequency of the quartz crystal in order to verify the rigid behavior of the polymer film deposited on the electrode¹⁸. Under no circumstances was a peak broadening observed, indicating that all polymer films under study are rigidly behaved.

The charge passed during the process was obtained by integration of the current measured. The electropolymerization process was continuously monitored and the results were sampled every 100 ms. The CV scan rate is fixed at 25 mV/s in all experiments.

Electropolymerization Results

The electrochemically induced cation-radical coupling mechanism commonly accepted for the electrosynthesis of doped conducting polypyrrole (1), shown in Scheme I, involves a step-

insert Scheme I

growth polymerization and requires two electrons to activate each monomer. Dimers and tetramers are shown, for example, but oligomers of all sizes are expected. Redox doping occurs at the potential used for polymer synthesis and, thus, the polymer forms in the charged state as an insoluble electrode supported film. This mechanism was substantiated by our earlier study in organic media¹². This mechanism is also valid in many aqueous electrolytes. A typical example is the electropolymerization of pyrrole using NaCl as an electrolyte to prepare poly(pyrrole chloride) (PP-Cl). Figure 1 shows the charge and frequency responses simultaneously recorded during a potentiostatic electropolymerization as the polymer deposits onto the electrode. An increase of charge is accompanied by the build-up of polymer on the electrode (frequency decrease). The linear relationships shown in these plots indicates that the polymerization proceeds at a constant rate.

Correlating the charge and the moles of polypyrrole repeat units deposited leads to a linear relationship, as shown in Figure 2. A 30% doping level of the polymer is assumed, based upon a

variety of previously reported experimental results¹⁹⁻²², in order to convert the mass of the polymer deposited into moles of repeat unit due to the fact that the polymer is partially oxidized when polymerized. This yields an effective molecular weight of 75.7 for each polymer repeat unit (1 pyrrole and 0.3 Cl). The apparent number of electrons involved for polymerization of each polypyrrole repeat unit, n , can then be calculated from the slope of the plot according to Faraday's law.

It should be noted that this treatment is based upon the assumptions that the electrosynthesized polymer is unsolvated and the electropolymerization is 100% efficient. Obviously, these assumptions are not strictly true. Solvation of the polymer will increase the mass deposited as a function of charge and give a high electropolymerization efficiency. The formation of soluble oligomers, on the other hand, lowers the electropolymerization efficiency as they diffuse into the bulk electrolyte. In our previous work in organic media, we find oligomer diffusion from the electrode surface to only affect the results in the early stages of electropolymerization. This is most likely due to the fact that, during the initial stages of electropolymerization, the redox and polymerization processes are occurring at a *metallic electrode*. As the electropolymerization proceeds, the electrode becomes covered with polypyrrole and subsequent redox and polymerization processes occur at a *conducting polymer electrode*. Strictly speaking, the calculated apparent n value serves for qualitative comparison. Interestingly, the experimentally measured apparent n value is reproducibly found to be between 2.2 to 2.5 during electrosynthesis of PP-Cl, which is in agreement with the 2.3 n value proposed by the cation-radical coupling mechanism which requires 2 electrons for the formation of polymer linkages via radical coupling and 0.3 electrons for the partial oxidation of the polymer backbone. These experimental results are highly reproducible and comparable n values are observed with many other electrolyte systems. Figure 3 shows the relationships between the electropolymerization charge and moles of polypyrrole repeat unit deposited during the electropolymerizations from sodium dodecyl sulfate (PP-DS), sodium poly(styrene sulfonate) (PP/PSS), and sodium copper phthalocyanine-3,4',4'',4'''-tetrasulfonate

(PP-CuTSP). These plots are linear and yield n values of ca. 2.2- 2.6. These observations lead us to believe that the impact of solvation and soluble oligomers on the overall apparent n value in these depositions are negligible. While it is possible that these effects may both be present, and offsetting one another, it seems unlikely given the extreme differences in the nature of the dopant species. These results also provide supportive evidence that cation-radical coupling is the overwhelmingly dominant electropolymerization mechanism.

Figure 4 shows the charge and frequency responses during the potentiostatic electropolymerization of pyrrole in 0.1M aqueous LiClO_4 solution to form poly(pyrrole perchlorate) (PP- ClO_4). The mass of the polymer increases non-linearly with time while, analogous to the results shown in Figure 1, the charge builds at a constant rate. This is substantially different from the expected behavior of an electrochemically activated step-growth polymerization process. Correlating charge and moles of pyrrole units polymerized during electropolymerization yields the results shown in Figure 5. Here, a doping level of 30% is again assumed based on compositional analysis. The non-linearity of the results indicates a variation in the number of electrons involved in the deposition of each polypyrrole repeat unit, or the electrochemical efficiency, during the polymerization. This makes the calculation of an average n value for the entire polymerization time meaningless. However, a close examination of the process reveals that three different stages are involved, as marked A, B, and C in Figures 4 and 5. In stage A, which spans up to 9-10s of polymerization time, approximately 1.6 electrons per polypyrrole repeat unit are involved ($n=1.6$). In stage B, over approximately a 5s time span, polymer deposition proceeds very rapidly with little charge transferred, only about 0.12 electrons per polypyrrole repeat unit are observed ($n = 0.12$). Although this stage is extremely short, a 3000 Hz (ca. 500 nm) film is deposited on the electrode. This quantity of deposition would take about 100 seconds to accomplish if the polymerization was carried out in a NaCl solution (Figure 2). In stage C, the charge versus time results become somewhat linear with an n value ranging from 2.5 to 2.8, resembling those observed in NaCl, NaPSS, and NaCuTSP solutions. Analyzing the conductance

peak width of the quartz crystal coated with a 5000 Hz PP-ClO₄ film, relative to a bare crystal, revealed no peak broadening indicating that the film is rigidly behaved. This eliminates the possibility that the large frequency change observed in stage B is an anomaly of the EQCM induced by the formation of a viscous polymer layer on the electrode which dampens the oscillations of the quartz crystal. These results strongly suggest that the polymerization proceeds by a mechanism different from cation-radical coupling.

The characteristics of the fast polymerization prompt us to propose that an electrochemically initiated chain polymerization, featuring a rapid chain growth and involving no redox processes, is involved in the early stages of film formation. Previously, only one study suggested that the electropolymerization of pyrrole may involve a free-radical polymerization when BF₄⁻ is used as the counteranion in organic media¹¹. The chain polymerization, as tentatively

insert Scheme II

illustrated in Scheme II, is believed to dominate stages A and B. This reaction may be initiated upon the electrochemical generation of some active species at the electrode surface, followed by rapid polymer chain growth which is characterized by a high polymerization rate and, thus, an exceptionally low apparent *n* value. Polymer 2, as a proposed product of the chain reaction, is believed to be formed during this phase of the electropolymerization. The fact that the polymer layer is insoluble and is difficult to isolate makes the characterization of the polymer difficult. Interestingly, the polymer formed on the electrode is electroactive, resembling regular polypyrrole. Wudl et al²³ have reported that electropolymerization of isothianaphthene in LiBF₄ leads to the formation of an unsaturated polymer (3), as illustrated in Scheme III, which was believed to occur

insert Scheme III

via a cationic chain polymerization. Jen and Elsenbaumer²⁴ have reported the synthesis of polyisothianaphthene (4) by oxidizing 1,3-dihydroisothianaphthene using O₂ and FeCl₃ (Scheme III). This suggests the possibility that the non-conjugated polymer (2) may undergo an oxidation on the electrode to become conjugated and ultimately form doped conducting polypyrrole (1). The

cation present during electropolymerization has little effect on the reaction, as confirmed by the fact that the same rapid deposition process is observed in a 0.1M NaClO₄ solution. Although the actual reactive species in the reactions are unknown, we speculate that the presence of ClO₄⁻ ion may activate the initial electrochemically generated species, and lead to a chain polymerization.

The dramatic changes that occur in the deposition rate, and the n value, during the polymerization lead us to believe there are several competitive processes occurring simultaneously. The cation-radical coupling process may be present during the entire polymerization, especially in stage C, though it seems to be overwhelmed by the chain reaction in stages A and B. This is distinguished by the linear frequency change-time relationship, and n value of close to 2.3, in the latter stages of reaction.

Figures 6 and 7 show the charge and frequency change to polymerization time relationships as a function of monomer concentration, respectively. The fact that the time required for the chain polymerization process to begin increases with decreasing monomer concentration, suggests that a build-up of reactive species at the electrode surface occurs. At some critical concentration the chain polymerization is initiated and the electrode is quickly coated with a polypyrrole film. Subsequent deposition occurs at a slower rate as expected for cation-radical coupling. At the lowest monomer concentration studied of 0.01 M, no chain deposition process is noted and, while 0.021 coulombs are passed, only a 469 Hz frequency change is noted. This correlates to an effective n value of 3.2 and suggests that while some film has been deposited (<75 nm), reactive species remain in solution. The fast deposition of the polymer film significantly reduces the monomer and reactive species concentration near the electrode surface, which consequently causes of the chain polymerization to cease. It should be noted that any possible change of monomer concentration, caused by the rapid polymerization, is transient and confined to the electrode surface. A change in bulk monomer concentration would not be detectable.

Figures 8 and 9 show the frequency change during potentiostatic polymerization and charge passed as a function of the number moles of polypyrrole repeat units during the

electropolymerization of pyrrole carried out in 0.1M NaBF₄ (PP-BF₄), Et₄NBF₄ (PP-BF₄), and KPF₆ (PP-PF₆), respectively. The non-linear, low n value, characteristics of these systems closely resembles those observed in ClO₄⁻ electrolytes. Again, there is little difference in results obtained with different counter-cations as evidenced by experiments carried out with NaBF₄ and Et₄NBF₄. Table 1 summarizes the results of electropolymerization of pyrrole in a series of electrolytes. It is interesting to note that the chain polymerization only occurs in aqueous solutions of ClO₄⁻, BF₄⁻, and PF₆⁻, which are non-nucleophilic, have a low level of hydration, and are comparable in size. Similar electropolymerizations of pyrrole were carried out using LiClO₄ and Et₄NBF₄ in MeCN and no chain polymerization was observed. This may suggest that the chain reaction results from strong interaction between solvent and electrochemically generated active species.

Electrochemical Switching Results

The presence of different electropolymerization mechanisms is expected to lead to formation of polymers with different properties which will, in turn, be reflected in their electrochemical behavior. In order to investigate the differences induced by possible structural changes, a 3000 Hz PP-ClO₄ film (*ca.* 500 nm), sampled at stage B where the polymer is thought to form via chain polymerization, along with a 10,000 Hz PP-ClO₄ film (*ca.* 1000-1500 nm), sampled at stage C where cation-radical coupling dominates, were studied. All of the films were thoroughly washed with distilled water to remove excess monomer and analyzed in monomer-free electrolytes. The results presented were obtained after cycling the films sufficiently to obtain reproducible current and frequency responses for multiple scans.

Figure 10 shows the current and frequency responses of a 3000 Hz film in monomer-free 0.1M LiClO₄ during a cyclic potential scan. The broad amperometric redox waves are common for a polypyrrole film on the large (*ca.* 1 cm²) working electrode employed in the EQCM. Of particular interest is the gravimetric response. An increase of frequency (*ca.* 65 Hz) occurs

commencing at -0.6V, when scanning anodically from -1.0 to -0.1V. Further scanning results in a substantial frequency decrease (ca. 160 Hz). This represents two different types of dominating ion transport, specifically cation and anion transport, and has not been observed in polypyrrole formed via cation-radical coupling which exhibits transport dominated by only one ionic species. The initial frequency increase, corresponding to a mass loss in the film, is believed to be due to the expulsion of cations (Li^+) from the film, while the frequency decrease thereafter is identified as a net mass gain resulting from incorporation of anions (ClO_4^-) into the film. The fact that both Li^+ and ClO_4^- are mobile species was further verified by the replacement of LiClO_4 with CsCl electrolyte. A dramatic change in the frequency response was observed as shown in Figure 11. As expected, the substitution of Li^+ with a heavier Cs^+ enhanced the frequency response correlated to cation transport, and replacement of ClO_4^- with a low mass Cl^- suppressed the frequency response during anion flux. It is commonly accepted that solvent will move into and out of electroactive polymer films during switching. For example, the Li^+ species is likely highly hydrated and this water of solvation will move with the ions. While this will complicate quantitative studies of ion transport (i.e., analysis of the magnitude of the frequency changes during switching) these comparative studies determine which ionic species dominates the ion transport process.

It is expected that the initial cation transport most likely results from the immobilization of ClO_4^- dopant anions within the film²⁵⁻²⁶. Thus, there are two types of ClO_4^- ions in the oxidized form of this 3000 Hz PP- ClO_4 film. One is immobilized in the film while the other is highly mobile and responsible for the anion flux in the polymer at higher potentials. This observation is in agreement with the conclusions reached by Mermilliod et al²⁷⁻²⁸ who employed AC impedance to study the redox processes of PP- ClO_4 films and found that two ionic species, termed "shallowly trapped" and "deeply trapped" ions, are involved. The initial oxidation activates the "shallowly trapped" species, further oxidation drives the "deeply trapped" ions out of the film. The cations that are expelled out of the film at low oxidative potentials in our observation may be interpreted as

the "shallowly trapped" ions as Mermiloid claimed and the mobile ClO_4^- which moves into the polymer at relatively high potentials can be correlated with the "deeply trapped" ions. Anion transport is quite common for a polymer doped with anions of high mobility such as ClO_4^- , however, the mechanism by which the ClO_4^- ions are immobilized in the polymer is unknown. We speculate that these ClO_4^- ions may interact with the polymer chains, and become physically entrapped during the chain polymerization. The fact that cation transport occurs at potentials lower than that used to activate the anion transport may suggest that the polymer domains containing these immobilized ClO_4^- are relatively free of defects and have longer conjugated chain lengths.

Figure 12 shows the current and frequency responses of the 10,000 Hz PP- ClO_4 film in monomer-free 0.1M LiClO_4 solution during a cyclic scan. The higher redox peak potential is caused by the potential drop across the more thickly polymer coated electrode. It is interesting to see the frequency response exhibits an uninterrupted anion flux with no sign of the cation transport that was observed in the 3000 Hz film. This significant difference in ion transport behavior of these polymers reveals that the electrochemical properties of these polymers are affected by the electropolymerization process. The chain polymerization yields polymers capable of cation transport, as the result of strong polymer- ClO_4^- interactions. The cation-radical coupling process, on other hand, leads to the formation of polymers exhibiting anion dominated transport behavior, which overwhelms cation flux in the polymer during redox switching.

Discussion

The presence of an electrochemically initiated chain polymerization of pyrrole in aqueous solutions of ClO_4^- , BF_4^- , and PF_6^- is proposed based on the fact that high polymerization rates, and exceptionally low n values, are observed during certain electropolymerization stages. These results cannot be interpreted in terms of the commonly accepted cation-radical coupling processes.

We have considered two other possible factors which could lead to low n values during polymerization, namely solvent influx and electrochemically induced oxidation of electrolyte.

Solvent incorporation tends to enhance the mass of the polymer film sensed by the EQCM, and thus decrease the apparent n value. It is highly unlikely that solvent incorporation causes the low observed n value in these experiments since no noticeable solvent incorporation is observed for electropolymerization of pyrrole in NaCl where the Cl^- ion is considered more highly solvated than the ClO_4^- ion²⁹. In addition, it is difficult to imagine that a major solvent influx would occur only in the initial stages of polymerization, and not throughout the entire polymerization process. If significant solvent incorporation did occur during electropolymerization, it would be expected in the latter stages of polymerization where the loose, porous structures of thick films are capable of trapping more solvent. Electrochemically induced chemical oxidation is also unlikely considering the well-known electrochemical stability of ClO_4^- (along with BF_4^- and PF_6^-) and the moderate experimental conditions under which the electropolymerization proceeds. A cyclic voltammetric background study performed in a monomer-free, 0.1M LiClO_4 revealed no signs of ClO_4^- decomposition. Mixing pyrrole and LiClO_4 solution yields no precipitation or color change. We observe no signs of oxidative reactions at low solution pH, excluding the possibility that the protons released during the polymerization may activate ClO_4^- to initiate chemical oxidations.

The mechanism of electrochemically initiated chain polymerization proposed in Scheme II only serves to illustrate the likely path along which the electropolymerization may proceed. The actual electrochemically related reactions may be more complicated and an accurate description of these processes is not possible at present. It has been reported that pyrrole can undergo acid-catalyzed polymerization³⁰ and the mechanism involved is highly controversial. We fully acknowledge that there are many possible mechanisms, for example, cationic, radical or charge-transfer complex polymerization, which may be occurring in these systems.

Conclusions

The electropolymerization of pyrrole in aqueous solution has been studied using the EQCM technique. A new mechanism for the electropolymerization of pyrrole, namely

electrochemically initiated chain polymerization, has been proposed to elucidate the complicated processes involved when the polymerization is carried out in aqueous ClO_4^- , BF_4^- , and PF_6^- electrolytes. This mechanism is distinguished by its remarkable features of a high deposition rate and exceptionally low n value. The subsequent electrochemical characterizations reveal that the polymer formed via chain polymerization exhibits both cation and anion dominated transport, while the polymer synthesized through cation-radical coupling is only capable of anion dominated transport.

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References

1. A. F. Diaz and J. Bargon, in *Handbook of Conducting Polymers*, T. A. Skotheim, Ed., Marcel Dekker Inc., New York 1986, Vol. I, pp. 81-115.
2. L. J. Buckley, D. K. Roylance, and G. E. Wnek, *J. Polym. Sci. B.*, **25**, 2179 (1987).
3. S. Kuwabata, K. Okamoto, and H. Yoneyama, *J. Chem. Soc. Faraday Trans. I*, **84**, 2317 (1988).
4. K. M. Cheung, D. Bloor, and G. C. Stevens, *J. Mat. Sci.*, **25**, 3814 (1990).
5. P. G. Pickup and R. A. Osteryoung, *J. Am. Chem. Soc.*, **106**, 2294 (1984).
6. M. Satoh, K. Kaneto, and K. Yoshima, *Synth. Met.*, **14**, 289 (1986).
7. M. Ogasawara, K. Funahashi, T. Demura, T. Hagiwara, and K. Iwata, *Synth. Met.*, **14**, 61 (1986).
8. K. M. Cheung, D. Bloor, and G. C. Stevens, *Polymer*, **29**, 1709 (1988).
9. B. L. Funt and S. V. Lowen, *Synth. Met.*, **11**, 129 (1985).
10. F. Beck, M. Oberst, and R. Jansen, *Electrochim. Acta*, **35**, 1841 (1990).

11. J. Prejza, I. Lundstorm, and T. Skotheim, *J. Electrochem. Soc.*, **129**, 1685 (1982).
12. C. K. Baker and J. R. Reynolds, *J. Electroanal. Chem.*, **251**, 307 (1988).
13. M. D. Ward and D. A. Buttry, *Sci. Rev.*, **249**, 1000 (1990).
14. M. R. Deakin and D. A. Buttry, *Anal. Chem.*, **61**, 1147 (1989).
15. G. E. Wnek, L. A. Prezyna, J. J. Lee, Y.-J. Qiu, and J. R. Reynolds, *Am. Chem. Soc., Div. Polym. Chem., Polym. Preprints*, **30** (2), 178 (1989).
16. L. A. Prezyna, G. E. Wnek, Y.-J. Qiu, and J. R. Reynolds, *Macromolecules*, in press.
17. C. K. Baker and J. R. Reynolds, *Synth. Met.*, **28**, 21 (1989).
18. R. Borjas and D. A. Buttry, *J. Electroanal. Chem.*, **280**, 73 (1990).
19. A. F. Diaz, J. I. Castillo, J. A. Logan, and W.-Y. Lee, *J. Electroanal. Chem.* **129**, 115 (1981).
20. P. Burgmayer and R. W. Murray, in *Handbook of Conducting Polymers*, T. A. Skotheim, Ed., Mercel Dekker Inc., New York 1986, Vol. I, pp. 507-523.
21. R. J. Waltman, A. F. Diaz, and J. Bargon, *J. Electrochem. Soc.*, **132**, 631 (1985).
22. K. J. Wynne and G. B. Street, *Macromolecules*, **19**, 2361 (1985).
23. F. Wudl, M. Kobayashi, and A. J. Heeger, *J. Org. Chem.*, **49**, 3383 (1984).
24. K.-Y. Jen and R. Elsenbaumer, *Synth. Met.*, **16**, 379 (1986).
25. Y.-J. Qiu and J. R. Reynolds, *Polym. Eng. & Sci.*, **31** 417 (1991).
26. C. K. Baker, Y.-J. Qiu, and J. R. Reynolds, *J. Phys. Chem.*, **24**, 678 (1991).
27. J. Tanguy and N. Mermiloid, *Synth. Met.*, **21**, 129 (1987).
28. N. Mermiloid and J. Tanguy, *J. Electrochem. Soc.*, **133**, 1073 (1987).
29. *Chemistry of the Elements*, N. N. Greenwood and A. Earnshaw, Ed., Pergamon Press Ltd., New York, 1984.
30. G. F. Smith, in *Advances in Heterocyclic Chemistry*, A. Katritzky, Ed., Academic Press Inc., New York, 1963.

Table 1. Electropolymerization of pyrrole in various aqueous electrolytes.

Poly(pyrrole anion) PP-A	Charge vs. Moles Repeat Unit Deposited	n value	Type of Electropolymerization
PP-Cl	linear	2.2 - 2.5	cation-radical coupling
PP-PSS	linear	1.8 - 2.2	cation-radical coupling
PP-DS	linear	1.8 - 2.3	cation-radical coupling
PP-CuTSP	linear	2.3 - 2.6	cation-radical coupling
PP-NO ₃	linear	2.2 - 2.5	cation-radical coupling
PP-CDS	linear	2.3 - 2.6	cation-radical coupling
PP-ClO ₄	non-linear	0.12 *	chain reaction
PP-BF ₄	non-linear	0.13 *	chain reaction
PP-PF ₆	non-linear	0.11 *	chain reaction

* The listed n values are calculated based on data from the B stages of the electropolymerization.

Figure Captions

- Figure 1. Charge and frequency responses for potentiostatic deposition of PP-Cl from a solution of 0.1M pyrrole and 0.1M NaCl.
- Figure 2. Charge vs. moles of PP-Cl repeat units deposited on the electrode during potentiostatic polymerization from a solution of 0.1 M pyrrole and 0.1 M NaCl.
- Figure 3. Charge vs. moles of polypyrrole repeat units deposited on the electrode. a) PP-CuTSP, b) PP-DS, c) PP/PSS.
- Figure 4. Charge and frequency responses for potentiostatic deposition of PP-ClO₄ from a solution of 0.1M pyrrole and 0.1 M LiClO₄.
- Figure 5. Charge vs. moles of PP-ClO₄ repeat units deposited on the electrode from a solution of 0.1M pyrrole and 0.1 M LiClO₄.
- Figure 6. Charge passed during potentiostatic deposition of PP-ClO₄ from a solution of 0.1M LiClO₄ and a) 0.01M, b) 0.03M, c) 0.07M, d) 0.1M pyrrole.
- Figure 7. Frequency responses during potentiostatic deposition of PP-ClO₄ from a solution of 0.1M LiClO₄ and a) 0.01M, b) 0.03M, c) 0.07M, d) 0.1M pyrrole.
- Figure 8. Frequency responses during potentiostatic deposition of polypyrrole from a solution of 0.1M pyrrole and 0.1M a) NaBF₄, b) Et₄NBF₄, c) KPF₆.
- Figure 9. Charge vs. moles of polypyrrole repeat units deposited from a) NaBF₄, b) Et₄NBF₄, c) KPF₆.
- Figure 10. Current and frequency responses of a 3000 Hz PP-ClO₄ film during a cyclic potential scan in 0.1M LiClO₄.
- Figure 11. Frequency responses of 3000 Hz PP-ClO₄ film during a cyclic potential scan in solutions of 0.1M a) LiClO₄ and b) CsCl.
- Figure 12. Current and frequency responses of a 10,000 Hz PP-ClO₄ film during a cyclic potential scan in 0.1M LiClO₄.

Fig. 1

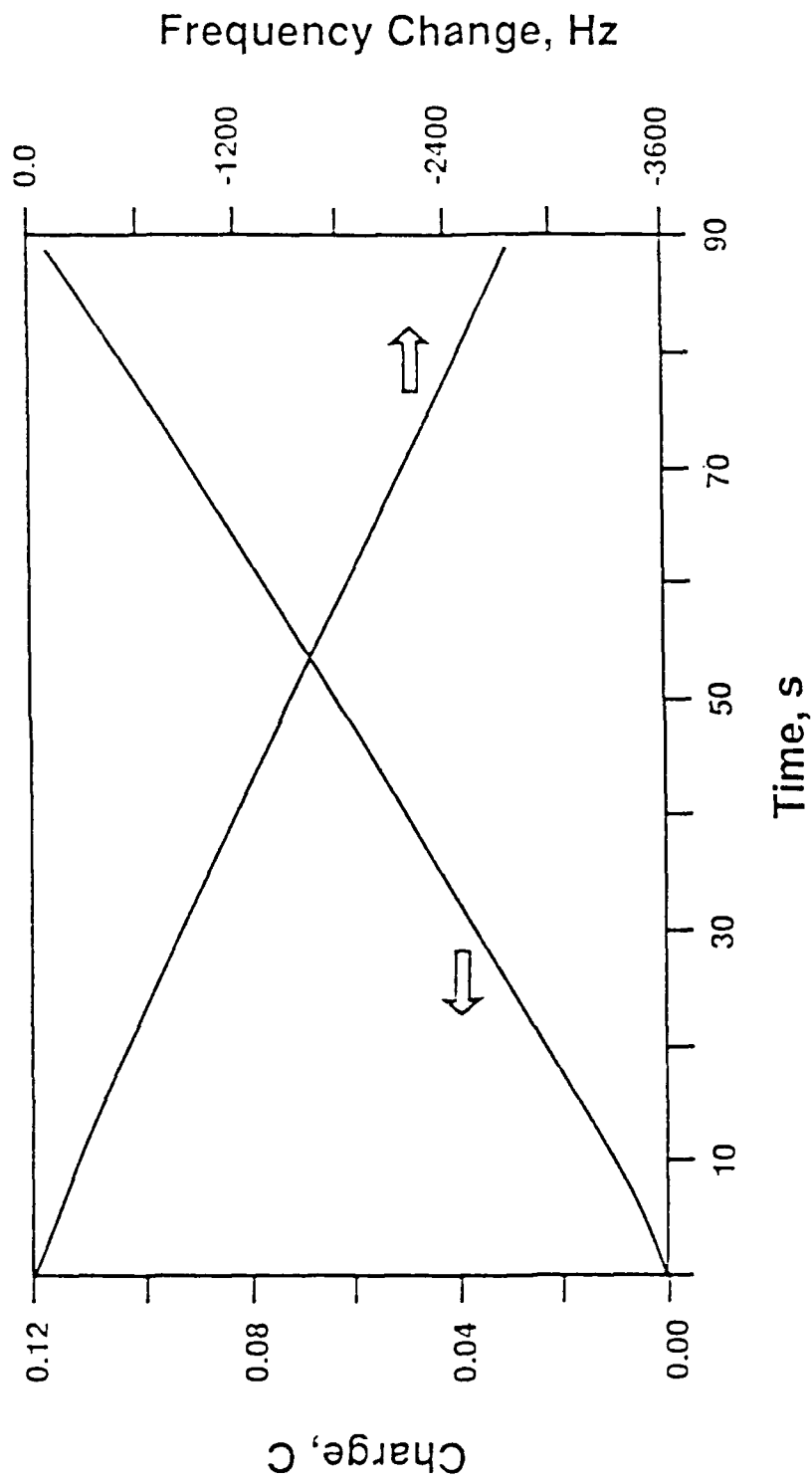


Fig. 2

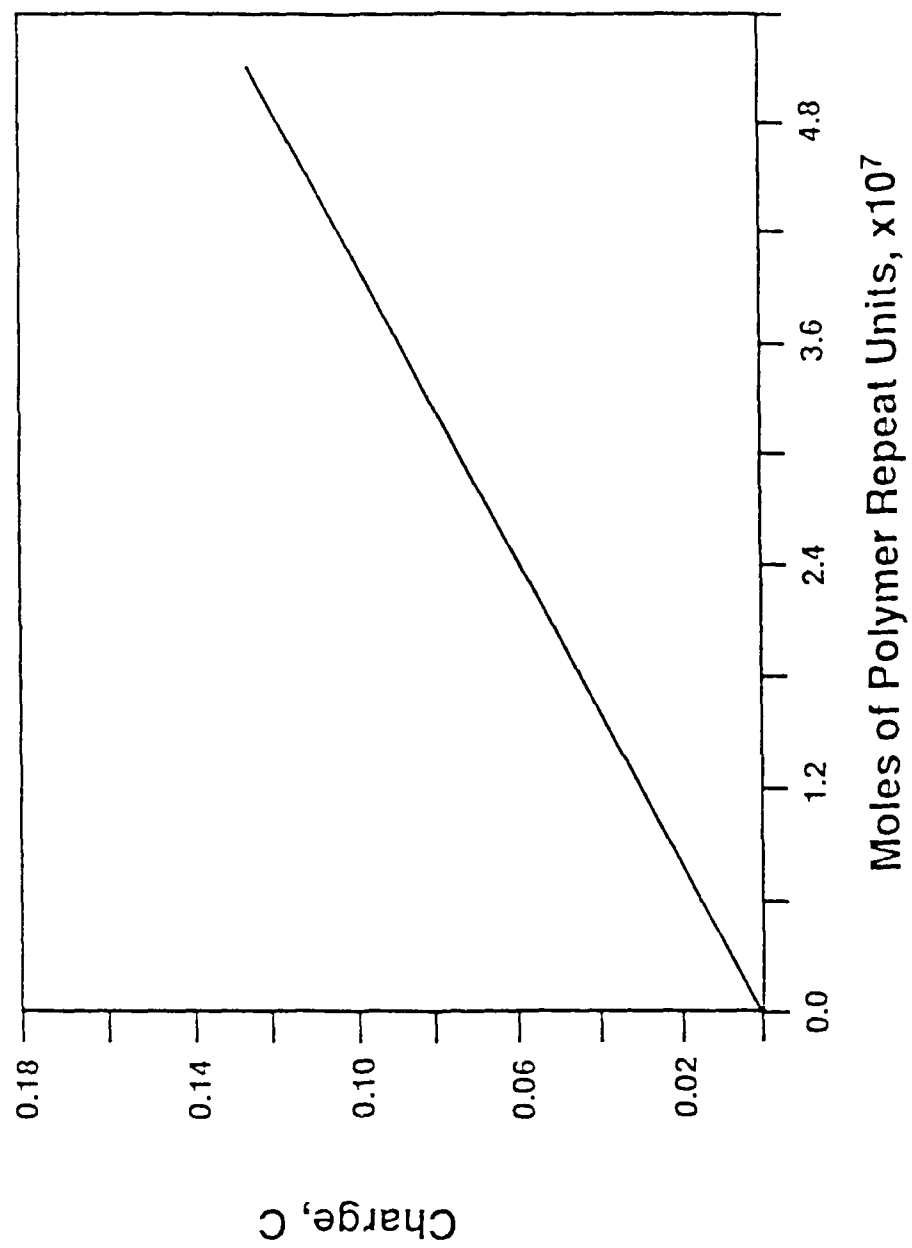


Fig. 3

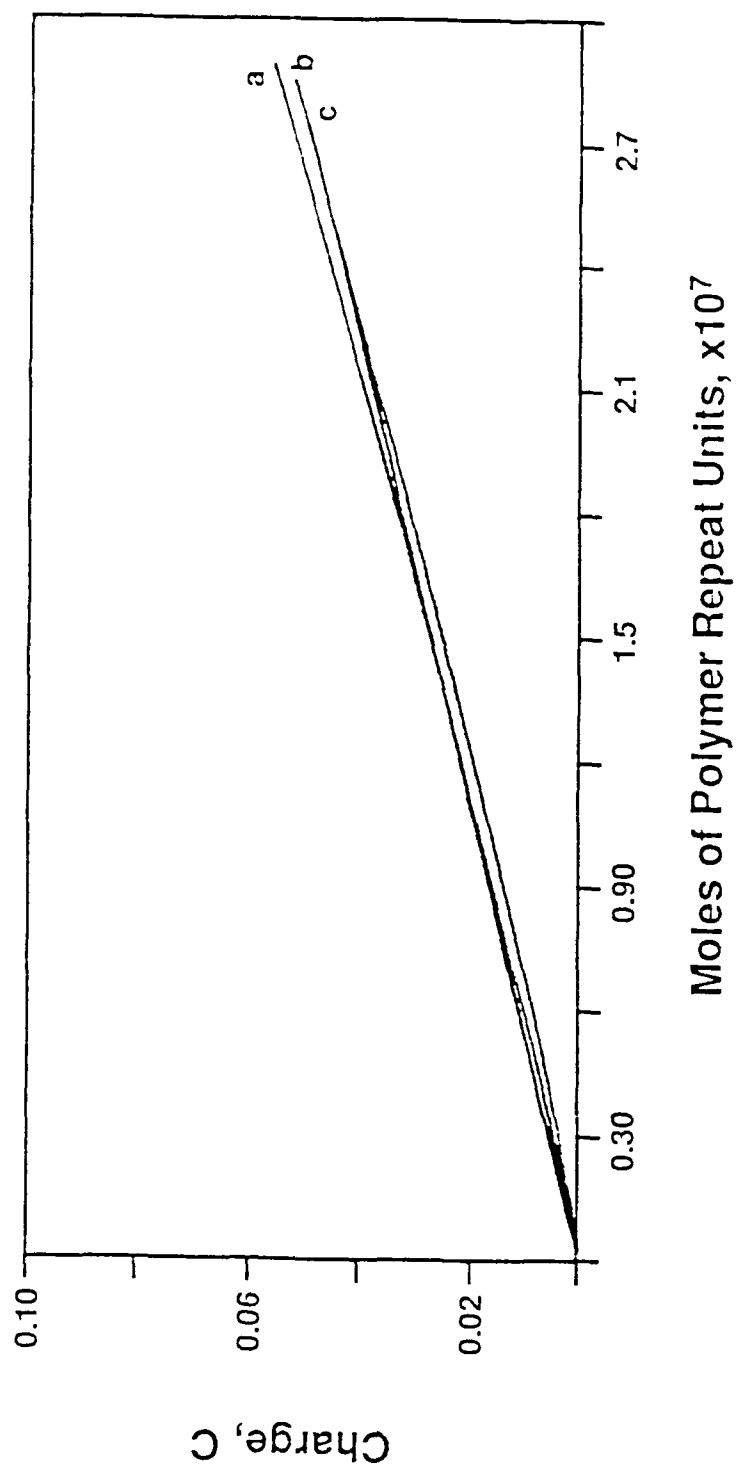


Fig. 4

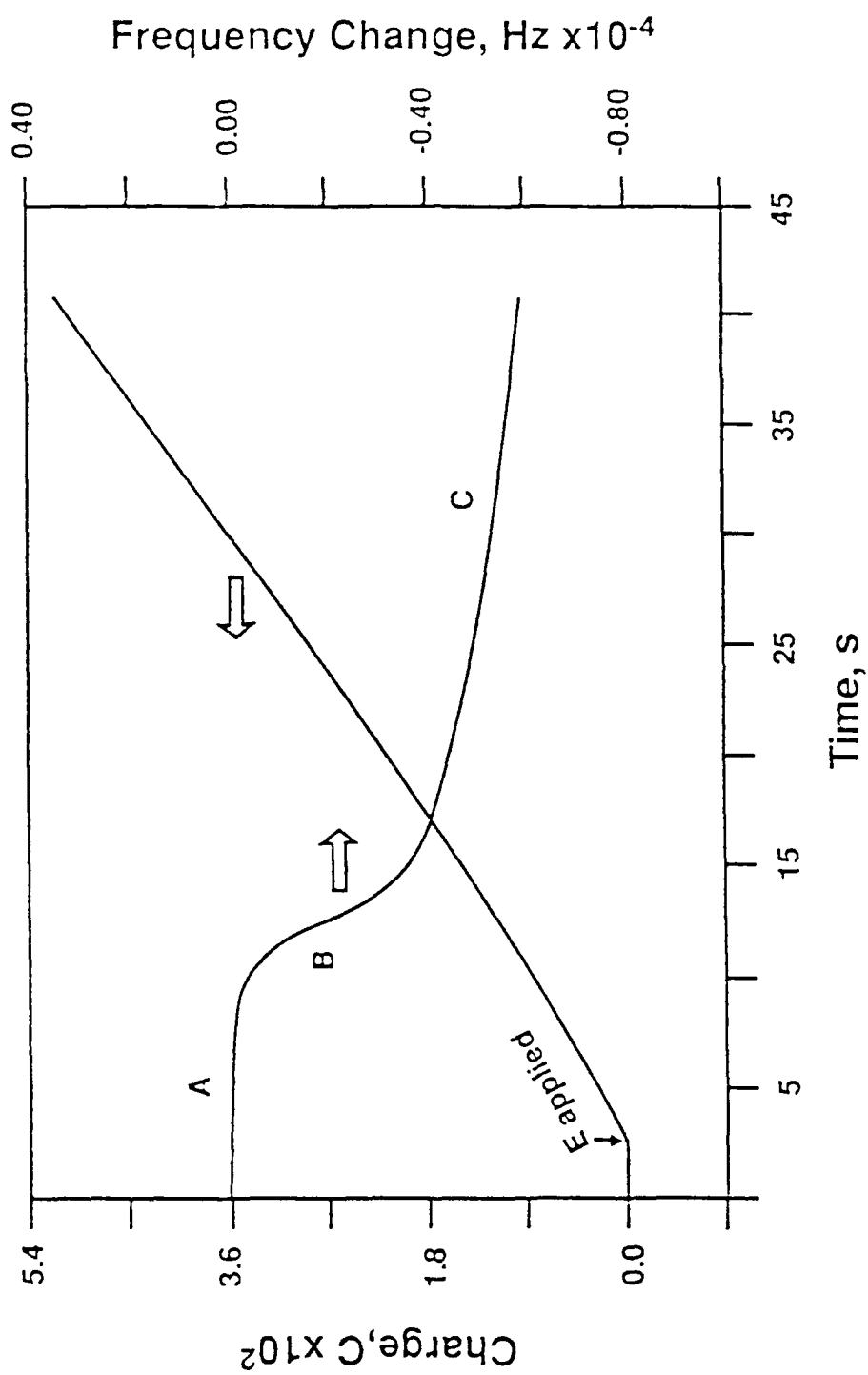
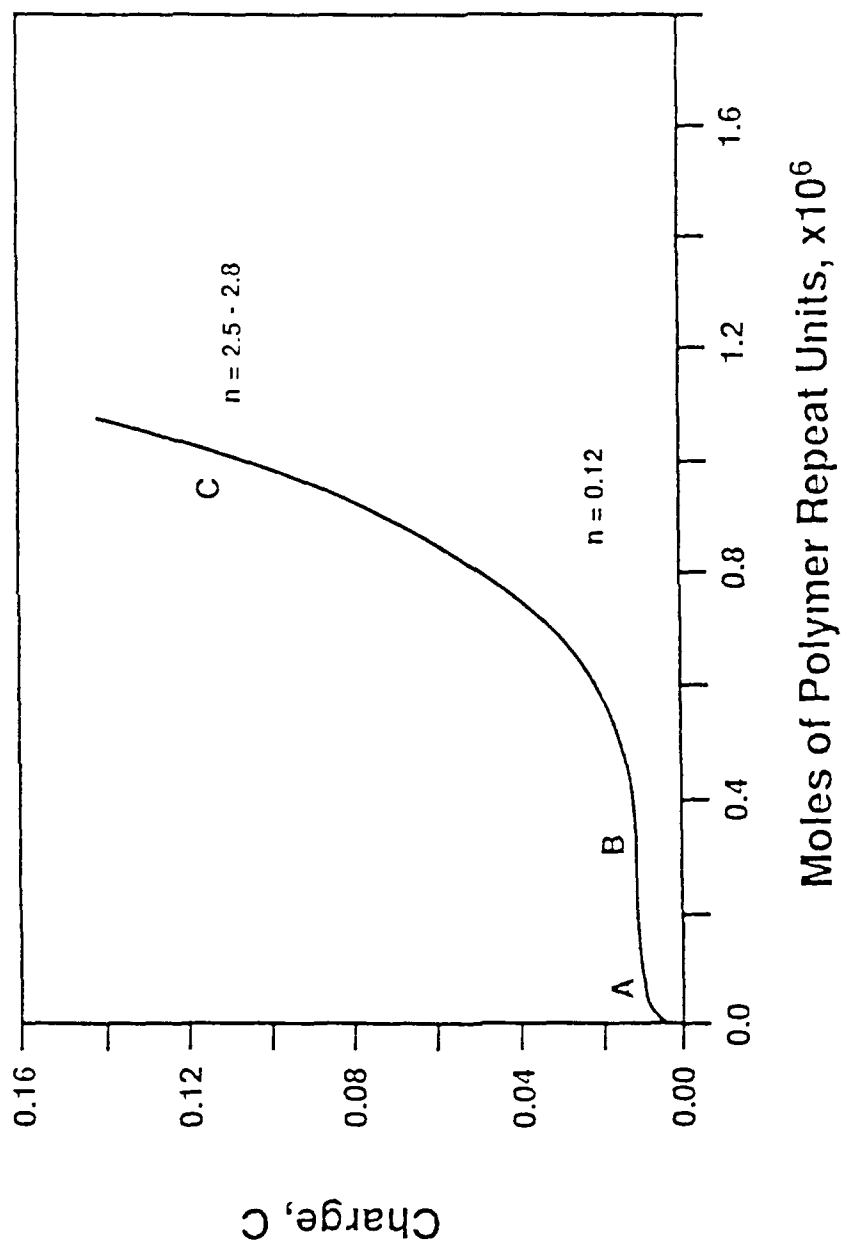
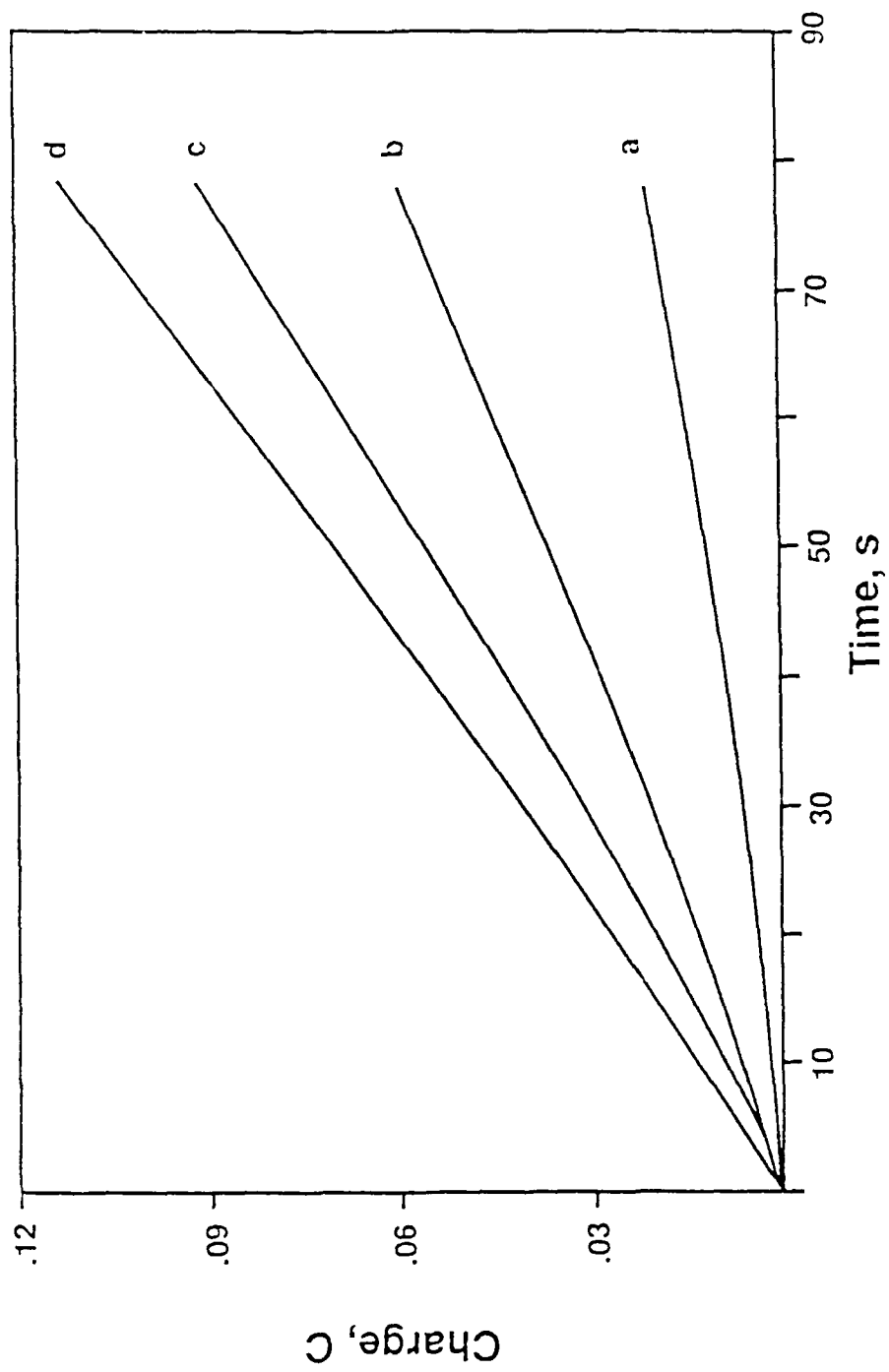


Fig 5



F₁₅ 6



F. 5 7

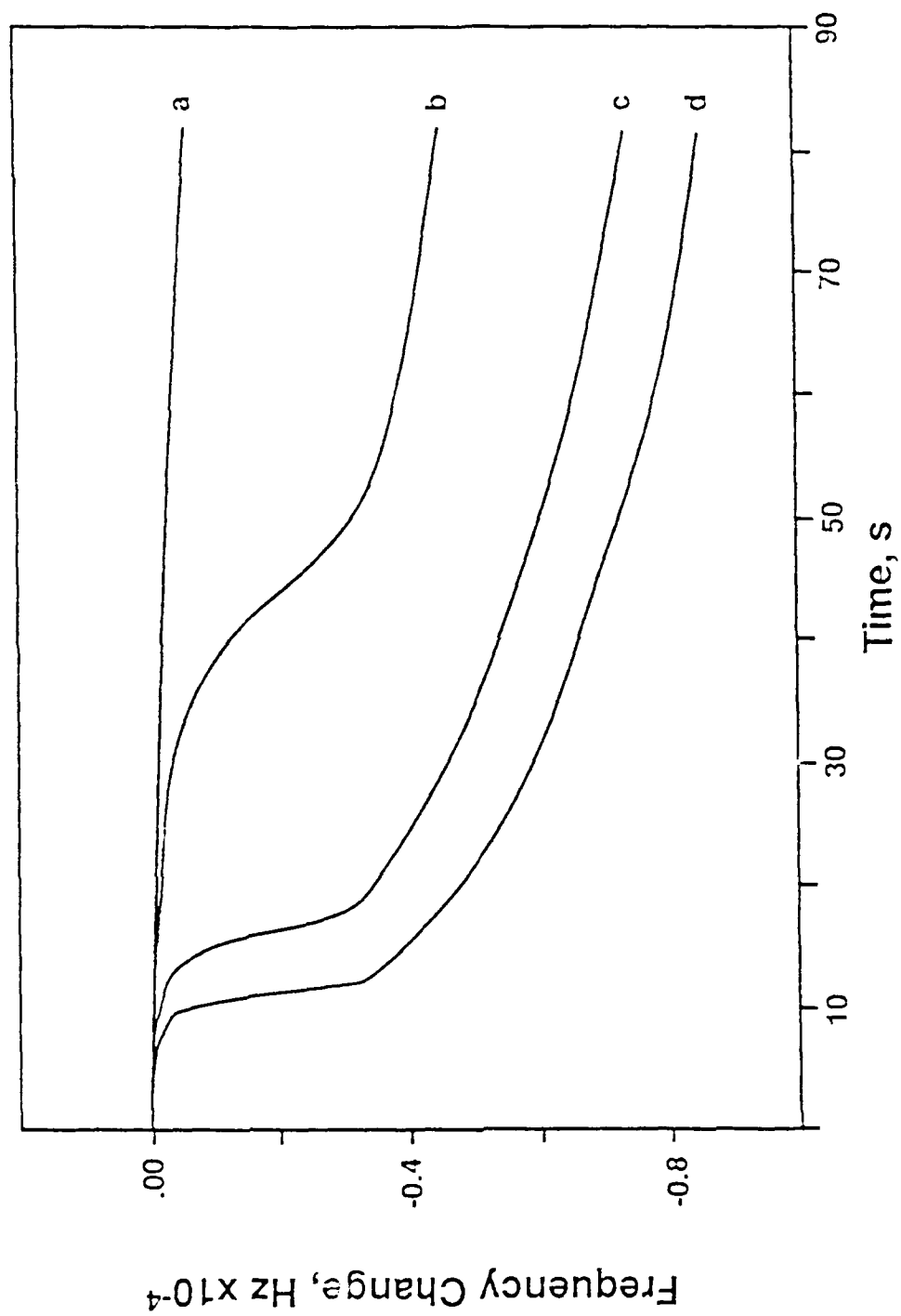


Fig 8

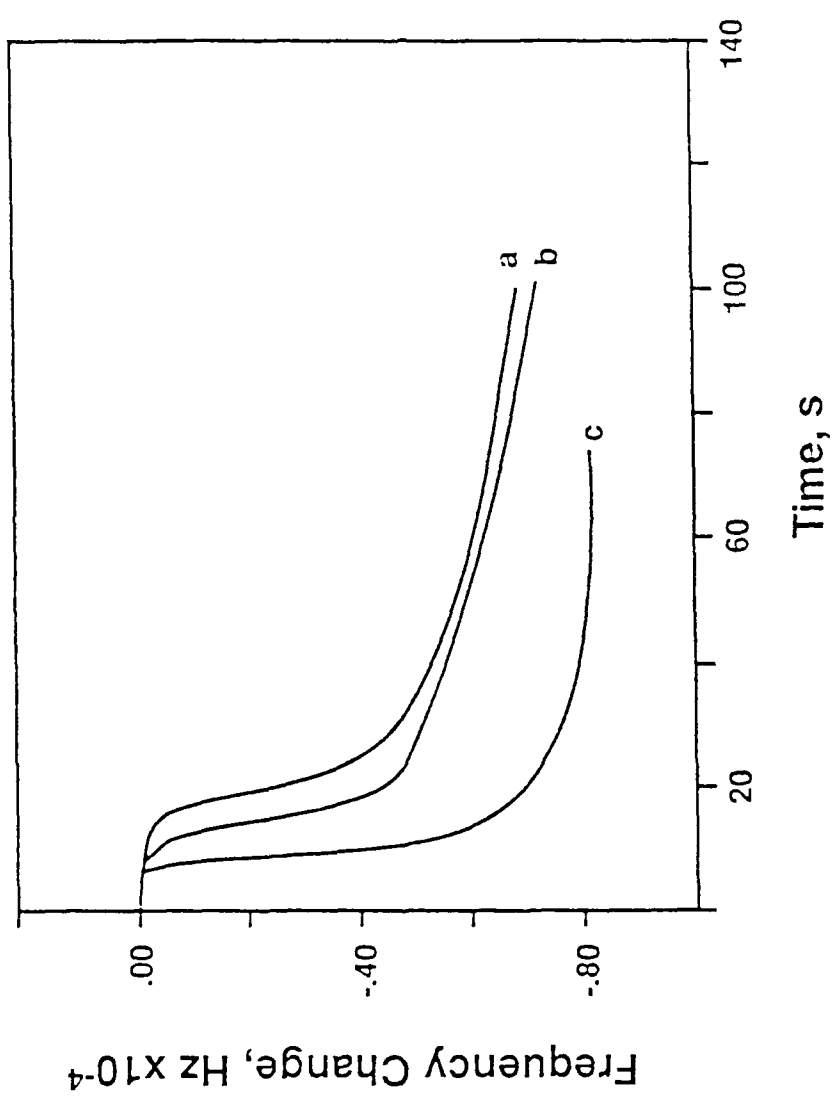


Fig 9

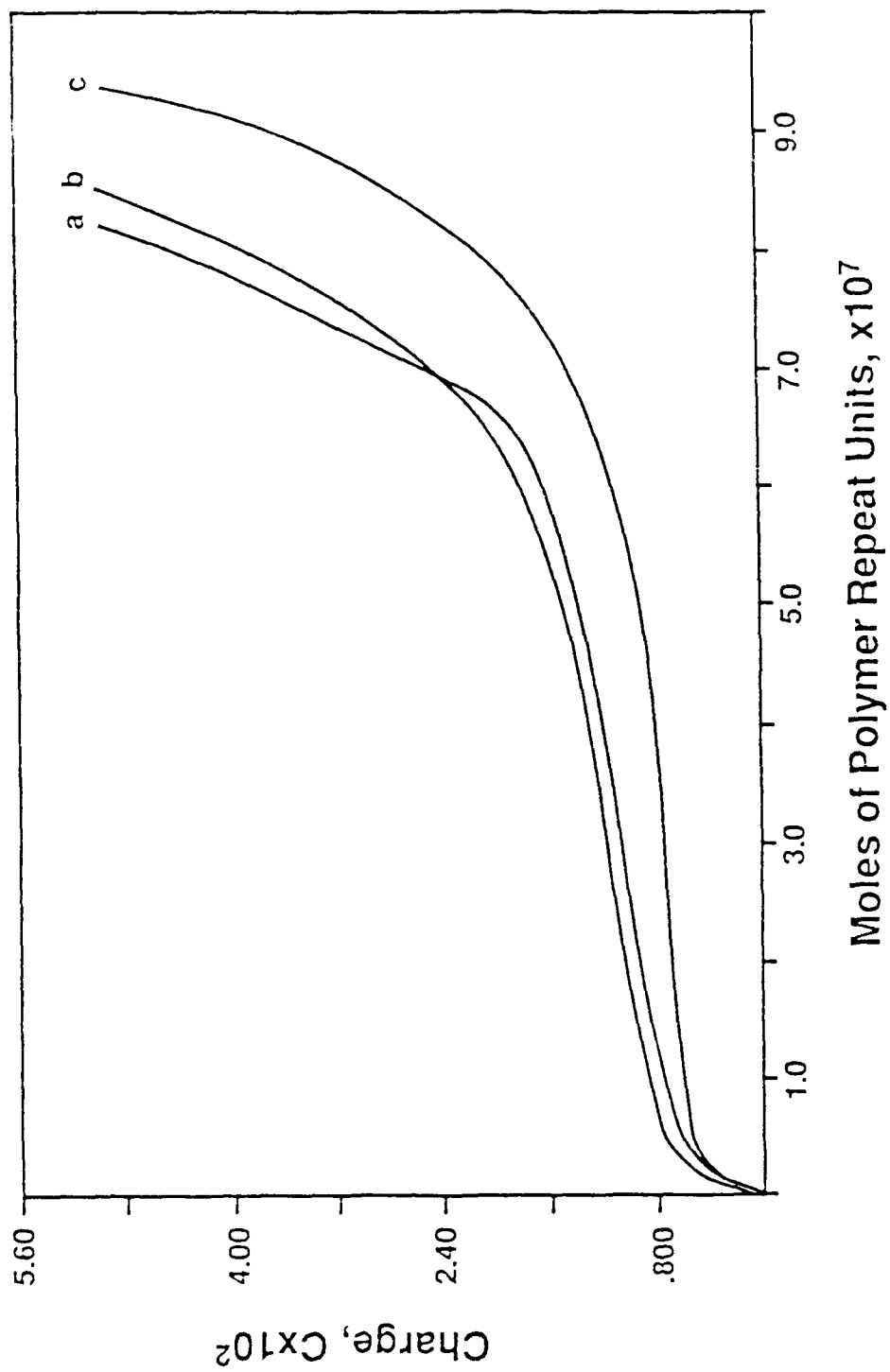


Fig. 10

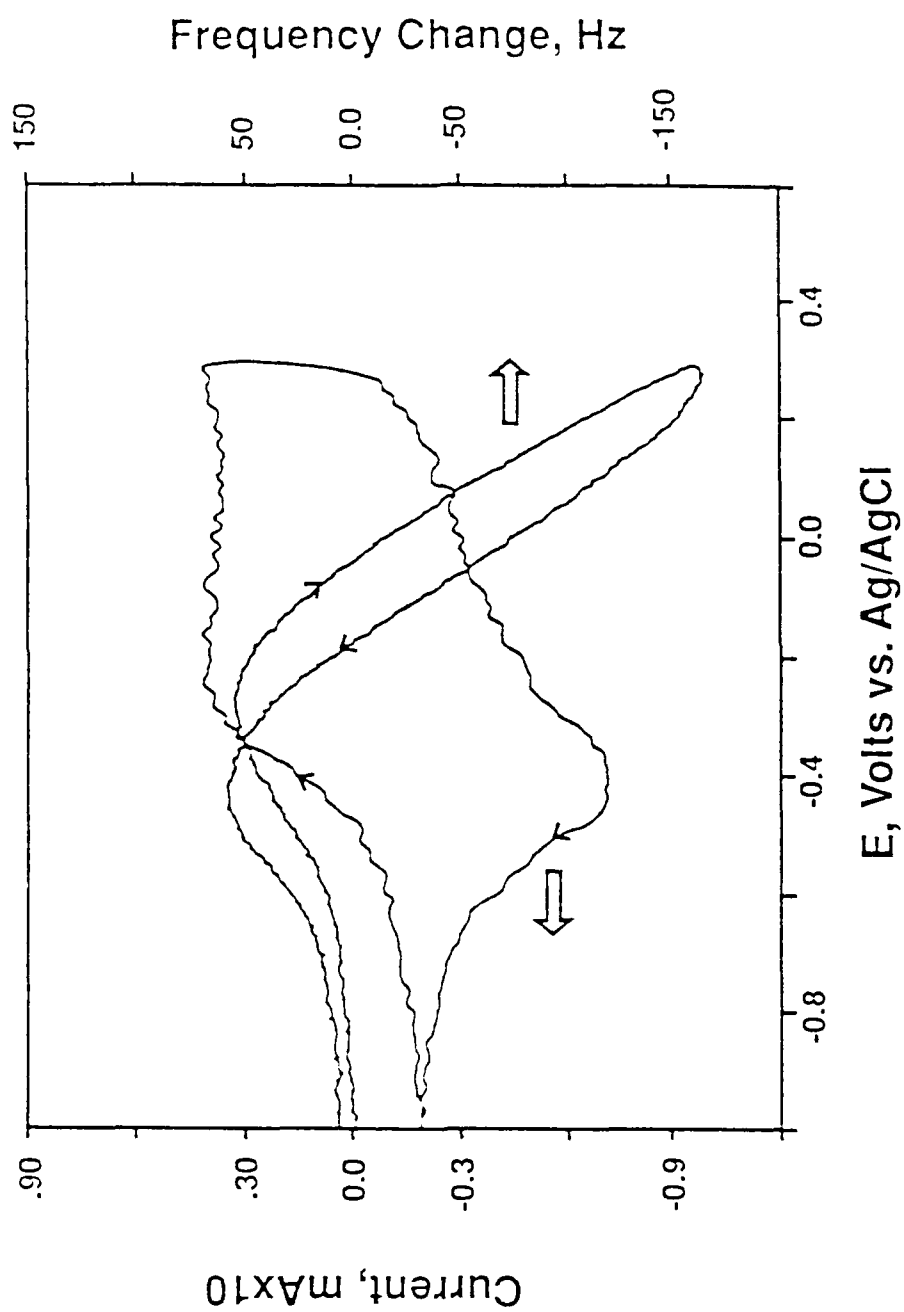


Fig. 11

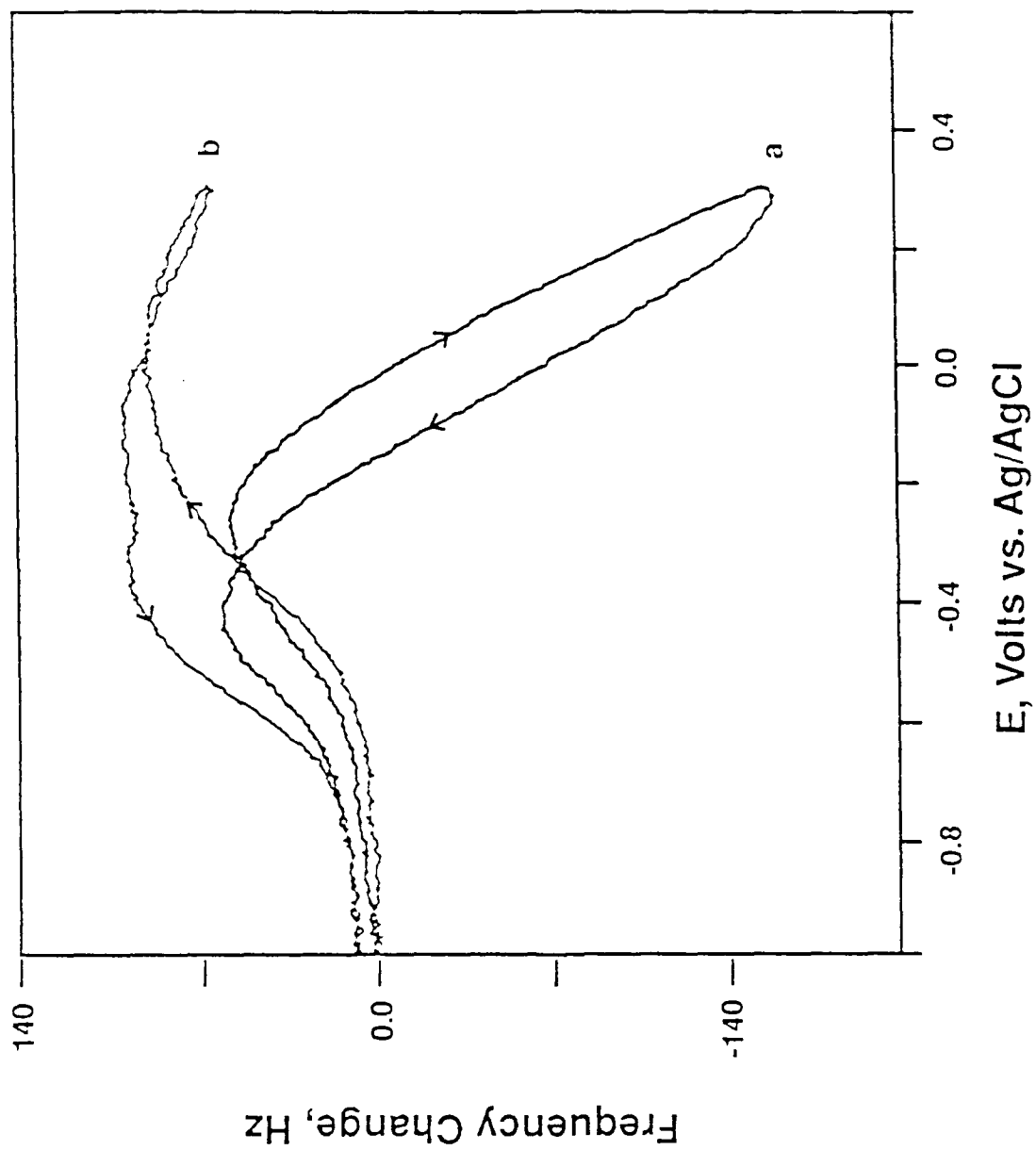
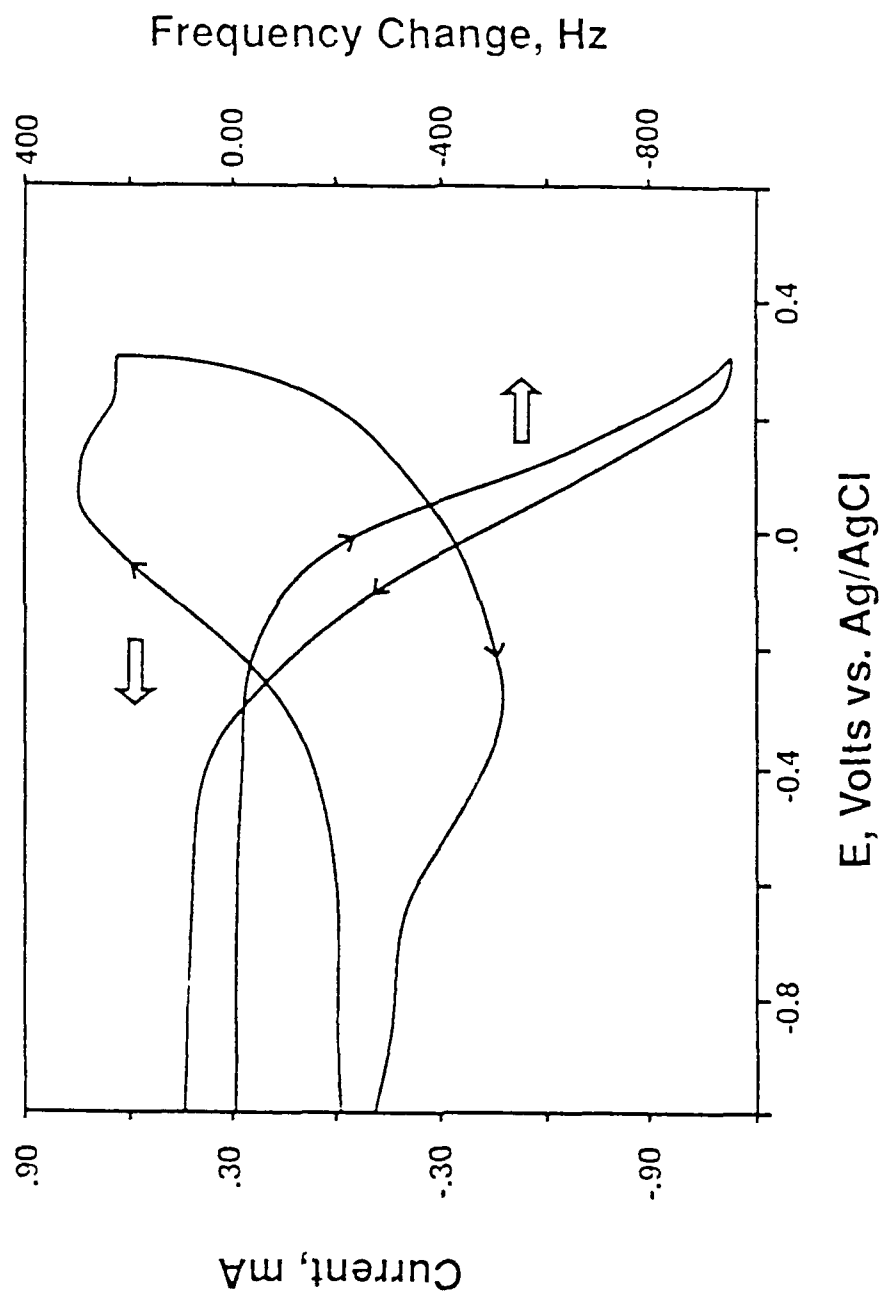
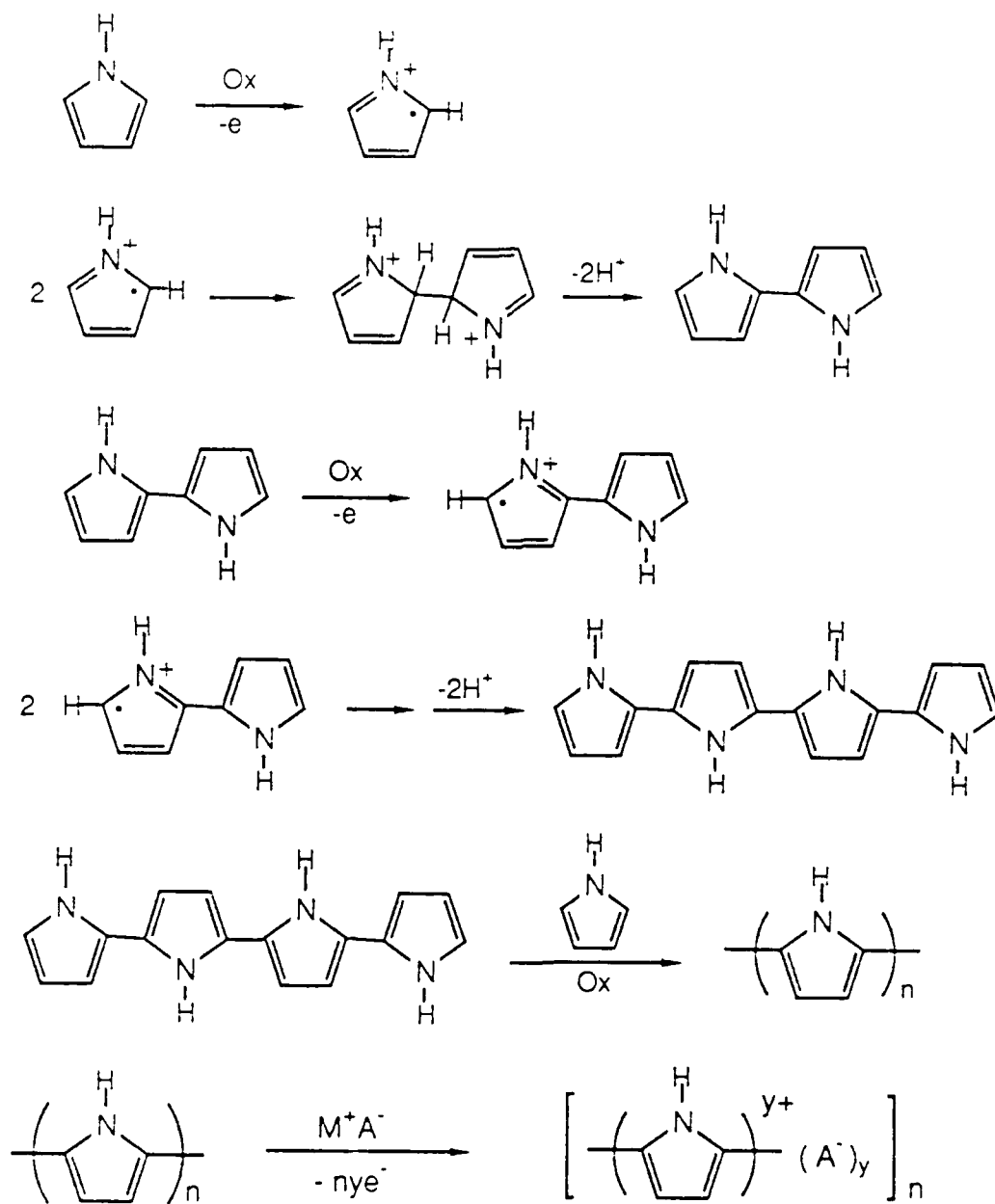


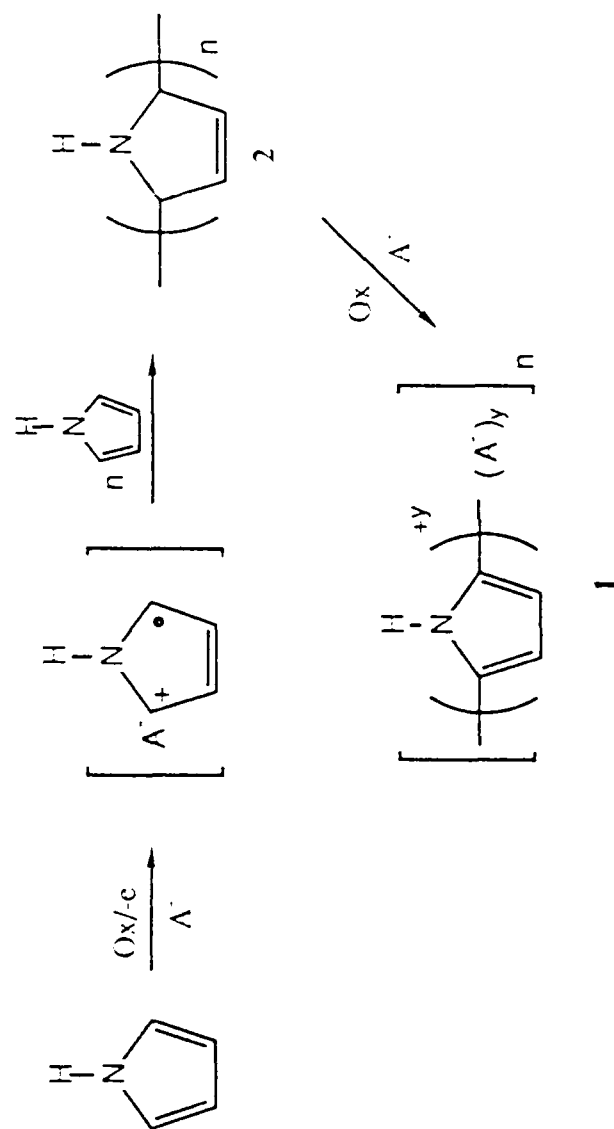
Fig. 12



Scheme 1



Scheme II



$A^+ = ClO_4^-, BF_4^-, PF_6^-$

Scheme III

